PB84-123793

Apportioning Light Extinction Coefficients to Chemical Species in Atmospheric Aerosol

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Research Triangle Park, NC

1983

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1. REPORT NO. EPA-600/J-83-122	2.	3 PB84-123793
4. TITLE AND SUBTITLE APPORTIONING LIGHT EXTINCTION COEFFICIENTS TO CHEMICAL SPECIES IN ATMOSPHERIC AEROSOL (Journal Version)		5. REPORT DATE 1983 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) H. Hasan and T. G. Dzubay		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N. C. 27711		10. PROGRAM ELEMENT NO. CDTA1D/01-1168 (FY-82) 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N. C. 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES
REF: Atmospheric Environment, 17(8):1573-1581, 1983

16. ABSTRACT

A 1978 Denver aerosol data set has been analyzed by a variety of methods for determining light scattering and extinction coefficients per unit mass concentration for specific chemical species in fine particles (<2.5 μm diameter). Multiple regression of light scattering coefficient versus chemical species concentrations was used to determine scattering to mass concentration ratios and their related uncertainties for specific chemical species, and the results are compared with those reported by previous investigators. Differences in the scattering to mass concentration ratios for all the major species in the aerosol except ammonium sulfate were found to be statistically insignificant. Calculations based upon size distributions were performed for both an assumed external and an internal mixture. An approximate expression for apportioning scattering coefficients by chemical species in an internal mixture was derived. It was found that while the type of mixture greatly affected the contribution of elemental carbon to light scattering, it had relatively little effect on the contribution to light extinction. Light scattering by non-absorbing species was nearly independent of mixture type. The extinction coefficients apportioned to specific chemical species using various models agreed with each other within a factor of two.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 10 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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EPA-600/J-83-122
JOURNAL ARTICLE

Atmospheric Environment Vol. 17, No. 8, pp. 1573–1581, 1983
Printed in Great Britain.

0004-6981/83 $3.00 + 0.00
Pergamon Press Ltd.

APPORTIONING LIGHT EXTINCTION COEFFICIENTS TO CHEMICAL SPECIES IN ATMOSPHERIC AEROSOL

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(*First received* 7 *June* 1982 *and in revised form* 18 *October* 1982)

Abstract—A 1978 Denver aerosol data set has been analyzed by a variety of methods for determining light scattering and extinction coefficients per unit mass concentration for specific chemical species in fine particles ($< 2.5\ \mu$m diameter). Multiple regression of light scattering coefficient versus chemical species concentrations was used to determine scattering to mass concentration ratios and their related uncertainties for specific chemical species, and the results are compared with those reported by previous investigators. Differences in the scattering to mass concentration ratios for all the major species in the aerosol except ammonium sulfate were found to be statistically insignificant. Light scattering and absorption coefficients were apportioned by chemical species for an external mixture using a published equation and for an internal mixture using equations that we derived. It was found that while the type of mixture greatly affected the contribution of elemental carbon to light scattering, it had relatively little effect on the contributions of non-absorbing species. Light absorption coefficients computed for external and internal mixtures were found to be highly dependent on the type of mixture. For light extinction coefficients, the contributions computed for chemical species were found to be nearly independent of mixture type. The extinction coefficients apportioned to specific chemical species using various models agreed with each other within a factor of two.

INTRODUCTION

The grayish-brown haze that appears over Denver, Colorado, popularly known as the "brown cloud", has been the subject of recent investigations. Interpretation of data taken during November and December 1978 revealed that the brown cloud in Denver was due mainly to the effects of fine particles which scatter and absorb light (Groblicki *et al.*, 1981; Sloane, 1983; Heisler *et al.*, 1980). Mass concentrations and chemical compositional data collected have been used to determine a light extinction budget by chemical species for the Denver aerosol. Light absorption due to particles was attributed to elemental carbon, while the light scattering was attributed to contributions from several chemical species, the major ones being ammonium sulfate, ammonium nitrate, elemental carbon and organic matter.

Groblicki *et al.* (1981) and Heisler *et al.* (1980) used different methods to apportion the light scattering coefficients to chemical species. Groblicki *et al.* (1981) performed a multiple regression of light scattering coefficients against mass concentrations of specific chemical species; the regression coefficients were assumed to represent the scattering coefficient per unit mass concentration of each chemical species. The regression coefficients differed, indicating a different light scattering efficiency for each chemical species. Heisler *et al.* (1980) examined data from three sites in addition to the site considered by Groblicki *et al.* (1981), and performed both stratification and regression analyses of the light scattering coefficient versus major chemical constituents of the fine particulate mass. Neither of Heisler's analyses refuted the assumption that all chemical species were equally efficient in scattering light. The contributions to the light extinction budget calculated under this assumption by Heisler *et al.* differed from those by Groblicki *et al.* by as much as a factor of 1.8 for some species.

In this work, two methods for apportioning scattering and extinction coefficients to various chemical species in an aerosol were examined with reference to the Denver aerosol. First, the multiple regression analysis of Groblicki *et al.* (1981) was repeated to determine the uncertainty in each regression coefficient. A second method consisted of theoretical calculations based on size distribution measurements of chemical species. Such measurements for the Denver aerosol were made by Countess *et al.* (1981) using cascade impactors. However, to perform calculations based on size distributions, information on the refractive indices and densities of individual aerosol particles is required. These properties are unknown for the Denver aerosol particles even though the bulk composition has been measured. In the absence of such information, we made calculations for two different cases. In one case, the aerosol was assumed to be a suspension of a variety of chemically pure individual particles. Such an aerosol will be referred to as an *external mixture*. In the second case, each particle in the aerosol was assumed to have a homogeneous composition identical to the bulk composition. Such an aerosol will be referred to as an *internal mixture*. [Other authors have defined internal mixtures as consisting of particles which are layered shells of pure species (Heintzenberg, 1979; Ackerman and Toon,

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1981) or of homogeneous particles which are allowed to change composition with size Sloane, 1983) but we do not use such definitions in this paper.] We derive an expression for the apportionment of light scattering to chemical species in an internal mixture and show that for non-absorbing aerosols the contribution of different chemical species does not change whether the mixture is internal or external. Elemental carbon scatters less if mixed internally than externally. However, it absorbs more in an internal mixture than in an external mixture, so that the total extinction coefficients per unit mass concentration for both mixtures are essentially the same. An extinction budget computed using scattering and absorption coefficients from the models mentioned above as well as with a constant coefficient per unit mass concentration, showed that the contributions to light extinction coefficient by specific chemical species are uncertain by a factor of two.

MATHEMATICAL PROCEDURE AND RESULTS

Multiple regression

We used the experimental data on mass concentrations M_{fi} of the major chemical species i in the fine fraction ($< 2.5\,\mu$m aerodynamic diameter) of Denver aerosol obtained by Countess *et al.* (1980) and the light scattering coefficients b_{sp} by Groblicki *et al.* (1981) to perform a multiple regression analysis using the equation

$$b_{sp} = a_0 + \sum_{i=1}^{5} a_i M_{fi}. \tag{1}$$

The regression coefficients a_i were assumed to be estimates of the scattering coefficient per unit mass concentration of each chemical species in the fine fraction. The five species included were ammonium sulfate, ammonium nitrate, elemental carbon, organic matter (defined as 1.2 times organic carbon) and the remainder (i.e. total fine particulate mass minus the sum of these species). The intercept in Equation (1) would be zero if b_{sp} varied linearly with the fine particle mass concentration and if light scattering by coarse particles were negligible.

We solved (1) by the least-squares method using the Statistical Package for Social Sciences, SPSS, (Nie *et al.*, 1975) on a UNIVAC 1100 computer. The values obtained for a_i were verified by repeating the computations using another statistical package (STAT/PACK) on the same computer. The analysis was done using data for 4-h measurements selected from the complete data set obtained by Countess *et al.* (1980) and Groblicki *et al.* (1981). We made our selection such that 4 h of concurrent data were available for each of the six parameters included in the model, resulting in 132 measurement periods. This is slightly less than the 157 measurement periods used by Groblicki *et al.* (1981), who made a selection such that at least 20 min of b_{sp} data were available during each hour in the 4-h averaging period. The values for M_{fi} averaged over the 132 measurement periods are given in Table 1. Groblicki's data on b_{sp} were obtained using a Model 1550 integrating nephelometer, which has an effective wavelength response of 475 nm (Ruby and Waggoner, 1981). Although both heated and unheated nephelometers were operated, only data from the heated nephelometer were used in our calculations. Thus, we did not consider effects due to relative humidity.

Table 1. Mean concentrations of major chemical species in Denver

Species	Fraction	Concentration $\mu g\,m^{-3}$	Percent M_f
Ammonium sulfate	fine	4.033	11.23
Ammonium nitrate	fine	5.825	16.22
Elemental carbon	fine	5.55	15.46
Organic matter	fine	7.84	21.83
Remainder	fine	12.69	35.34
Elemental carbon	coarse	1.7	

Values of the regression coefficients a_i and their 95% confidence limits are given in Table 2; the results of Groblicki *et al.* (1981) are presented for comparison. The slight differences between our results and those of Groblicki *et al.* arise from the different number of data points used in each case. The square of the correlation coefficient is $r^2 = 0.94$. Although the coefficients a_i for ammonium nitrate, organic matter and elemental carbon are numerically different from each other, their indicated uncertainties are sufficiently large that the differences are not statistically significant. However, the coefficient for ammonium sulfate is significantly larger than the others. The intercept obtained in the multiple regression is $a_0 = -0.016\,km^{-1}$. Such an intercept is not of major importance since its value is comparable to that for Rayleigh scattering and is less than 3% of the maximum value of b_{sp} in the data set.

Size distribution-based calculations

We computed values of light scattering coefficient per unit mass concentration from aerosol size distribution measurements using the relation (Willeke and Brockmann, 1977; Lewis, 1981; Ouimette and Flagan, 1982)

$$b_{sp}/M_f = I(n, k, D_g, \sigma_g, \lambda)/\rho \tag{2a}$$

where

$$I(n, k, D_g, \sigma_g, \lambda) = \int_0^{+\infty} \frac{1.5 Q_s(n, k, D/\lambda)}{D} f(D, D_g, \sigma_g)\,dD. \tag{2b}$$

Here, $Q_s(n, k, D/\lambda)$ is the Mie scattering efficiency for a single particle with refractive index $n + ik$, density ρ and diameter D; λ is the wavelength of the scattered light. The mass distribution function $f(D, D_g, \sigma_g)$ is taken to be log-normal with a geometric standard deviation σ_g and median D_g (Kerker, 1969). The latter

Table 2. Scattering coefficient per unit mass concentration from different statistical and mathematical models for $\lambda = 475$ nm

Component	Units	Multiple regression		Size distribution: External mixture		
		Previous work*	Present results	Measured distribution†	Average distribution¶	Internal mixture
Ammonium sulfate	$m^2 g^{-1}$	5.9	5.8 ± 1.0	3.4	3.2	3.2
Ammonium nitrate	$m^2 g^{-1}$	2.5	2.4 ± 0.6	3.7	3.8	3.8
Elemental carbon	$m^2 g^{-1}$	2.8	3.0 ± 2.9	3.2	3.3	−0.7
Organic matter	$m^2 g^{-1}$	3.9	3.7 ± 2.2	4.6§	4.2§	4.2§
Remainder	$m^2 g^{-1}$	1.5	1.7 ± 0.5	3.3§	3.5§	3.5§
Constant (a_0)	km^{-1}	−0.015	−0.016			

* Groblicki *et al.* (1981). These numbers differ from the published values by a normalization factor of 0.89 needed for a calibration correction. This factor is also contained in the present results.

† Each species has the size distribution parameters indicated in Table 3.

¶ All species have the same value of $D_g = 0.236\,\mu m$ and $\sigma_g = 2.12$ for their size distribution parameters.

§ The uncertainties in ρ and n indicated in Table 3 give uncertainties in the scattering coefficient per unit mass concentration of $\pm 1.4\,m^2 g^{-1}$ for organic carbon and $\pm 0.9\,m^2 g^{-1}$ for the remainder.

represents the volume-weighted mean diameter of the particle volume distribution and is related to the mass mean aerodynamic diameter D_a and specific gravity S through the relation

$$D_g = D_a(C_a/C_g S)^{1/2} \tag{3}$$

where the C's are the slip correction factors (Friedlander, 1977). The computer program of Dave (1968) was used to compute the scattering efficiencies $Q_s(n, k, D/\lambda)$. It should be noted that, although the above equations are strictly valid only for spherical particles, we shall be using them for the Denver aerosol particles which may be irregular.

External mixture. For the case of an external mixture, the total light scattering coefficient is the following superposition of the light scattering coefficients for each particle type (Ouimette and Flagan, 1982)

$$b_{s\rho} = \sum_i M_{fi} I(n_i, k_i, D_{gi}, \sigma_{gi}, \lambda)/\rho_i. \tag{4}$$

Equation (4) is of the same form as (1) with $I(n_i, k_i, D_{gi}, \sigma_{gi}, \lambda)/\rho_i$ corresponding to a_i and $a_0 = 0$. The scattering coefficient per unit mass concentration for each chemical species i was calculated using (2) and (3). Values for D_a and σ_g for each chemical species were taken from the measurements of Countess *et al.* (1981), and are shown in Table 3. For each species these values are the means of the corresponding values measured by Countess *et al.* (1981) for low, intermediate and high pollution days. Values for ρ, n and k for ammonium sulfate and ammonium nitrate (see Table 3) were taken from Weast (1976). Ammonium nitrate is birefringent, and the value for n shown is an unweighted average of its three values of refractive index. For organic matter the values of ρ and n were estimated to be typical of non-volatile hydrocarbons. Their uncertainties are substantial, because the mixture of organic compounds in Denver aerosol is unknown. For elemental carbon, published values range from 1 to $2.25\,g\,cm^{-3}$ for density, and from 1.56–0.47i to 2.75–1.46i for refractive index (Roessler and Faxvog, 1980; Weast, 1976). Such ranges are partly due to varying porosity in graphitic carbon. Because the effects of porosity on density and refractive index tend to cancel when $b_{s\rho}$ is computed, values for ρ, n and k should be chosen so that all are determined for the same sample of carbon. Such a determination was made by Janzen (1980) for carbon black, and the resulting values are shown in Table 3.

We evaluated the mean density $\bar{\rho}$ of the remainder as the volume-weighted average using the formula

$$\bar{\rho}^{-1} = \sum_i c_i/\rho_i \tag{5}$$

Table 3. Physical constants and parameters of volume (or mass) size distributions of specific chemical substances

Component	Assumed mixture	Refractive index	Density $g\,cm^{-3}$	D_a μm	D_g μm	σ_g
Ammonium sulfate	External	1.52	1.77	0.36	0.255	2.10
Ammonium nitrate	External	1.55	1.725	0.32	0.229	1.87
Elemental carbon	External	1.97–0.65*i*	1.85	0.28	0.190	1.87
Organic matter	External	1.5 ± 0.1	1.2 ± 0.2	0.33	0.296	2.53
Remainder	External	1.58 ± 0.05	1.9 ± 0.3	0.32	0.215	2.12
	Internal	$1.59 - 0.089i$	1.64	0.32	0.236	2.12

where

$$c_i = M_{fi} / \sum_i M_{fi} \tag{6}$$

and the subscript i refers to the components of the remainder, identified by Countess *et al.* (1980) as soil, water, trace elements, lead salts and non-sulfate sulfur. This formula, which we derived for immiscible liquids, was assumed to apply to the Denver aerosol. The average refractive index $\bar{n}$ was calculated from (Ouimette and Flagan, 1982)

$$\bar{n} = \bar{\rho} \sum_i c_i n_i / \rho_i. \tag{7}$$

The mass concentrations M_{fi} used in (6) were taken from the measurements of Countess *et al.* (1980), while ρ_i and n_i were taken from Weast (1976). Since the size distribution parameters of the remainder or of all the associated species were not available, we took D_g and σ_g for the remainder to be the mass concentration-weighted means of the corresponding parameters (Table 3) for the four major species. The average density $\bar{\rho}$ was used to calculate D_g using (3). The average values are given for the remainder in Table 3. The uncertainties in $\bar{\rho}$ and $\bar{n}$ are our estimates to account for lack of knowledge of the exact values for the various components of the remainder.

The results for the scattering coefficients per unit mass concentration are given in Table 2. For organic carbon and the remainder, the uncertainty introduced by the ignorance of the correct values of ρ and n was estimated and is shown in the final footnote of Table 2. It is worth noting that small uncertainties in ρ and n produce an almost 35% uncertainty in the scattering coefficients per unit mass concentration.

To determine the effect of the size distributions on these results, we repeated the above calculation using a single size distribution having the average values $\bar{D}_g = 0.236\,\mu$m and $\bar{\sigma}_g = 2.12$ for all chemical species. The results are presented in Table 2. A comparison of these numbers with the corresponding ones in the previous column reveals that the effect of replacing the experimental size distributions by the average one is small. In no case is this effect greater than 6%.

Internal mixture. The assumption of an internal mixture implies that each chemical species has an identical value of D_g as well as of σ_g. Although there are differences among experimentally determined values of D_g and σ_g in Table 3, the values are close enough for consideration of the approximation of an internal mixture as a limiting case. For the assumption that Denver aerosol was internally mixed, we based our computations on size distributions for which values of $\bar{D}_g$ and $\bar{\sigma}_g$ were taken to be mass concentration-weighted means of the corresponding quantities for specific chemical species. The contribution to the light scattering coefficient for each chemical constituent in an internal mixture was extracted as follows.

First note that the integral in (2), which is plotted in Fig. 1, varies approximately linearly with n for $1.5 \lesssim n \lesssim 1.9$ and $0.35 \lesssim D_g/\lambda \lesssim 0.7$. The contribution to the integral owing to k is nonlinear as illustrated in Fig. 2 and will be denoted by $\gamma(n, k, D_g, \sigma_g, \lambda)$. For fixed values of D_g/λ, and σ_g, we thus have

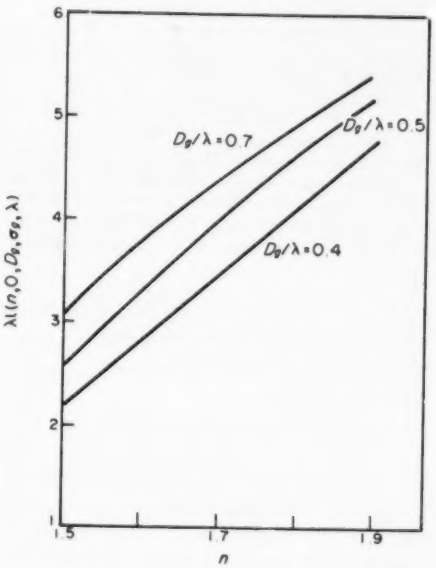

Fig. 1. Variation of $\lambda I(n, 0, D_g, \sigma_g, \lambda)$ with n for various values of D_g/λ, and $\sigma_g = 2.12$.

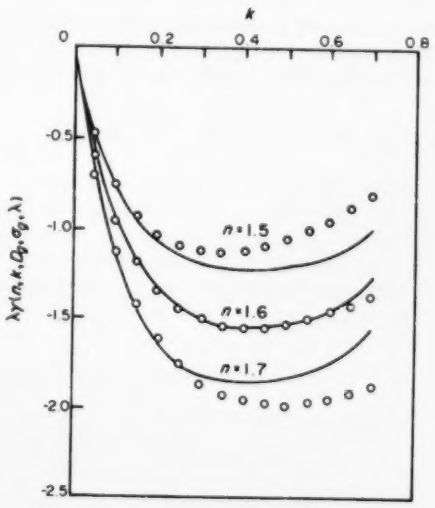

Fig. 2. Variation of $\lambda\gamma(n, k, D_g, \sigma_g, \lambda)$ with k and n for $D_g/\lambda = 0.5$ and $\sigma_g = 2.12$. The open circles represent the theoretically calculated values, while the smooth curves are plots of the equation $\lambda\gamma(n, k) = (1 - 0.9n)(28.8k - 91.7k^2 + 133.3k^3 - 75.5k^4 + 0.04)$.

$$I(n, k, D_g, \sigma_g, \lambda) \cong \alpha n + \beta + \gamma(n, k, D_g, \sigma_g, \lambda) \quad (8)$$

where α, and β depend on D_g, λ and σ_g. The density $\bar{\rho}$ and the real part of the refractive index $\bar{n}$ for the internal mixture are assumed to be given by Equations (5)–(7), where the summation now extends over the four major species as well as the remainder. After substituting (5)–(8) into (2a) and simplifying, we obtain

$$b_{sp} = \sum_i M_{fi} I(n_i, 0, \overline{D}_g, \bar{\sigma}_g, \lambda)/\rho_i + M_{fe}\delta \quad (9)$$

where,

$$\delta = \frac{M_f}{M_{fe}} [I(\bar{n}, \overline{k}, \overline{D}_g, \bar{\sigma}_g, \lambda) - I(\bar{n}, 0, \overline{D}_g, \bar{\sigma}_g, \lambda)]/\bar{\rho}. \quad (10)$$

Here $\overline{k}$ is the imaginary part of the refractive index for the internal mixture, and M_{fe} is the elemental carbon fine mass concentration. If none of the species has a complex index of refraction, then $\delta = 0$ and Equations (4) and (9) are identical if D_g and σ_g in (4) for each chemical species are replaced by $\overline{D}_g$ and $\bar{\sigma}_g$. From the results for the external mixture in Table 2 we see that this is an excellent approximation. Thus, for a non-absorbing aerosol the results for internal and external mixtures are essentially identical under the approximations made here.

For an aerosol that absorbs light there are at least two methods in the literature for computing $\overline{k}$. One prescription is the volume averaged index (Ouimette and Flagan, 1982)

$$\overline{k} = \bar{\rho} \sum_i c_i k_i/\rho_i. \quad (11)$$

Another prescription for $\overline{k}$ is

$$\overline{k} = \bar{\rho}\,\bar{n} \sum_i c_i k_i/(\rho_i n_i) \quad (12)$$

which is a generalized version of an expression for a two-component mixture (Chylek *et al.*, 1981). Use of either formula for $\overline{k}$ causes δ to be nonlinear in M_{fi} and it is not generally feasible to express linearly the contributions by chemical species. However, the contributions by chemical species can be expressed approximately linearly under the following conditions: (a) elemental carbon is the only absorbing species, and its mass concentration is less than 20%, as is the case in Denver, (b) $\overline{k}$ is evaluated using (11), and (c) the function in Fig. 2 is used to solve the expression in brackets in (10).

The results for an internal mixture were computed under these conditions and are shown in Table 2. For non-absorbing species the results for external and internal mixtures are essentially the same. However, for elemental carbon in an internal mixture, the coefficient becomes $-0.7\,m^2\,g^{-1}$. The negative number is a surprising result with the implication that adding carbon to the aerosol would decrease light scattering. However, it should be emphasized that this result pertains to the case of each particle containing less than 20% elemental carbon concentration. (For pure elemental carbon particles the scattering coefficient is a positive number.) Moreover, the sign of the coefficient is sensitive to the manner in which $\overline{k}$, $\bar{n}$ and $\bar{\rho}$ are completed. For example, if $\overline{k}$ is evaluated using (12), the coefficient for elemental carbon comes out to be $0.3\,m^2\,g^{-1}$, a small positive number. In any case, the contribution of elemental carbon to scattering is smaller for an internal mixture than an external mixture. This is consistent with the results of other authors (Ackerman and Toon, 1981; Heintzenberg, 1979) who have compared the scattering from carbon and sulfate in an external mixture and a carbon core surrounded by a sulfate shell. They find less scattering and greater absorption for the second case than for the first. Incidentally, a multiple regression analysis involving scattering coefficients measured in Denver using an *unheated* nephelometer produced a negative scattering coefficient for elemental carbon which was dismissed as unphysical (Sloane, 1983). In the present calculation for an internal mixture a possible negative contribution to scattering by elemental carbon is not necessarily unphysical since the scattering coefficient for the complete particle is positive.

Total light scattering coefficient per unit mass concentration

Table 4 gives results on total light scattering coefficient per unit mass concentration obtained both theoretically using different mathematical models as well as experimentally for various wavelengths of light. The first case shown represents the ratio of the averages of the measured values of the scattering coefficient and the fine particulate mass concentration for the 132 measurement periods considered in this paper. The second row gives the concentration-weighted average computed from (4) assuming the aerosol to be an external mixture.

The next three rows of values in Table 4 were calculated for the aerosol assumed to be an internal mixture. The first was calculated with the values of the physical parameters given in the last row in Table 3 and corresponds to the assumption that $\overline{k}$ is given by (11). A second set of values was obtained by using all the same parameters as before except that (12) was used for evaluating $\overline{k}$. As we can see from the table, the values for the scattering coefficient per unit mass concentration agree within 4% for the two assumptions.

The third result for an internal mixture takes into account the possible porosity of carbon-containing aerosol particles. In fact, recent examination of fine particles in Denver by electron microscopy revealed agglomerates of irregularly shaped particles having void spaces within them (Russell, 1979). The effect of porosity on the density and refractive index of the internal mixture was estimated from (Medalia and Richards, 1972; Janzen, 1979)

$$\rho' = (1 - \Phi)\bar{\rho} \quad (13)$$

$$n' = (1 - \Phi)\bar{n} + \Phi, \qquad k' = (1 - \Phi)\overline{k} \quad (14)$$

Table 4. Ratios of scattering coefficient to fine fraction mass concentration deduced under assumption of species independence

(b_{sp}/M_f), $m^2\,g^{-1}$					
$\lambda = 475$ nm	$\lambda = 530$ nm	$\lambda = 550$ nm	Reference	Location	Method
2.49			*	Denver	Ratio of measured means
3.64	3.05	2.86	†	Denver	Theoretical external mixture average (Table 2)
3.04	2.57	2.42	†	Denver	Theoretical internal mixture ($\bar{n} = 1.59$, $\bar{k} = 0.089$, $\Phi = 0$)
3.18	2.69	2.53	†	Denver	Theoretical internal mixture ($\bar{n} = 1.59$, $\bar{k} = 0.072$, $\Phi = 0$)
3.13	2.65	2.49	†	Denver	Theoretical internal mixture ($\bar{n} = 1.59$, $\bar{k} = 0.089$, $\Phi = .25$)
	3.5		††	Houston	Ratio of measured means
	2.78		§	Northwest	Measured ratio

* Present analysis of data by Groblicki *et al.* (1981) and Countess *et al.* (1980).
† This work.
†† Dzubay *et al.* (1982).
§ Waggoner and Weiss (1980). Measurements at five locations in northwest U.S.A. The value given here is smaller than the published value by a factor of 1.13 introduced to take into account a temperature correction inadvertently omitted by Waggoner and Weiss (Lewis, 1981).

where Φ represents the volume fraction of void spaces in the particle. The size distribution of the particles was assumed to have the same values of $\overline{D}_a$ and $\bar{\sigma}_g$ as before, but $\overline{D}_g$ was computed from Equation (3) using the density obtained from Equation (13). As the value of Φ is increased, b_{sp}/M_f increases slightly until it reaches a maximum, after which it starts decreasing. Results are given in Table 4 for $\Phi = 0.25$, for which b_{sp}/M_f is a maximum. The resulting value is less than 4% higher than the value for $\Phi = 0$, which indicates that the amount of void space has relatively little net effect on the light scattering coefficient per unit mass concentration. The wavelength dependence of b_{sp}/M_f is approximately $\lambda^{-1.65}$ for the external mixture and approximately $\lambda^{-1.5}$ for the three internal mixtures considered.

The theoretically calculated results for external and internal mixtures are within 15% of each other, but they are 28–46% higher than the ratio of measured means. A possible explanation of the difference is that the size distribution of aerosol particles whose scattering coefficient is measured by the heated nephelometer differs significantly from that measured by cascade impactors (and used for theoretical calculations) because of the evaporation of moisture. We can illustrate this effect by assuming a 50% water content, the evaporation of which would cause a 21% reduction in D_a. Thus smaller diameter results in values for b_{sp}/M_f which agree within 17% with the measured value. Alternatively, the higher theoretical value could be caused by use of inappropriate values of ρ and n for some chemical species. If we take the lower limits of the coefficients for organic carbon and the remainder (footnote, Table 2), the resulting ratios b_{sp}/M_f agree within 15% of the measured value. Incidentally, the ratio of measured means using the value of b_{sp} from the unheated nephelometer is $3.91\,m^2\,g^{-1}$. Although this agrees with the theoretical ones, the comparison is not meaningful because the ratio is based upon b_{sp} measured under humid ambient conditions, while the mass measurements were taken under dry laboratory conditions.

In the last lines of Table 4 we give the values obtained by Dzubay *et al.* (1982) for Houston, Texas and Waggoner and Weiss (1980) for five locations in northwestern U.S.A. The values for Denver are within the same range as those obtained elsewhere by these investigators.

Absorption coefficient per unit mass concentration:

The fine particle absorption coefficient b_{apf} is affected by different assumptions about the nature of the aerosol. Since the only absorbing species is elemental carbon, we shall be concerned with $(b_{apf}/M_f)_e$; the size distribution based calculations give a value of $10.5\,m^2\,g^{-1}$ at $\lambda = 475$ nm for an internal mixture with the parameters given in Table 3. The corresponding value is $5.5\,m^2\,g^{-1}$ for an external mixture. At $\lambda = 550$ nm, the results are 8.9 and $4.9\,m^2\,g^{-1}$ for internal and external mixtures, respectively. The wavelength dependence of $(b_{apf}/M_f)_e$ is thus $\lambda^{-0.7}$ for pure carbon black, while it is $\lambda^{-1.1}$ for an internal mixture. Groblicki *et al.* (1981) determined the absorption coefficient at 550 nm by measuring light transmission through filter-collected aerosol. They performed a linear regression of the measured absorption coefficient b_{ap} versus the fine and coarse elemental carbon mass; the result was $(b_{apf}/M_f)_e = 12.5\,m^2\,g^{-1}$. McClenny and Rohl (1981) recently suggested that the presence of non-absorbing particles causes the light transmission method to overestimate b_{ap}; for the Denver data of McClenny and Rohl the overestimate was a factor of 1.6. Clarke (1982) arrived at a similar conclusion on the basis of theoretical and experimental

estimates, and found that b_{ap} could be overestimated by as much as a factor of 1.3. Whether or not the measured absorption coefficient per unit mass concentration reported by Groblicki *et al.* is adjusted by such a factor, the measured value is much closer to the value calculated for an internal mixture than for an external mixture. Although this appears to indicate that the aerosol mixture in Denver was internal and not external, such a conclusion is highly dependent upon the parameters used to describe elemental carbon. For example, Sloane (1983) assumes that the refractive index and density of elemental carbon in an external mixture are 1.7–0.8i and $1\,g\,cm^{-3}$ and obtains an absorption coefficient for fine particle elemental carbon of $9.3\,m^2\,g^{-1}$ for $\lambda = 0.55\,\mu m$. Such a result is almost double our value for an external mixture and is about the same as our result for an internal mixture.

Extinction coefficients per unit mass concentration

The contribution of each species to the total extinction of light (excluding humidity effects) was computed based on the different models described above. The extinction coefficient b_{ext} was calculated as the sum

$$b_{ext} = b_{sp} + b_{ap} + b_{ag} + b_R. \qquad (15)$$

The absorption coefficient b_{ap} was due to a fine particle component b_{apf} and a coarse particle component b_{apc} ($b_{apc} = 3.8\,C_{aec}\,m^{-1}$), where C_{aec} is the mass concentration of the coarse elemental carbon in $g\,m^{-3}$ (Groblicki *et al.*, 1981). The contribution to b_{ag} was taken to be entirely from NO_2 concentrations. We used the value $b_{ag} = 0.015\,km^{-1}$ given by Groblicki *et al.* (1981) for $\lambda = 550\,nm$. The Rayleigh scattering coefficient was taken to be $b_R = 0.010\,km^{-1}$, which is the value for standard air at 0°C for $\lambda = 550\,nm$ (Penndorf, 1957) corrected for the elevation of Denver.

The percentage contributed to the total extinction coefficient b_{ext} for light of wavelength 550 nm for each chemical species was evaluated using (15) and various models for apportioning b_{sp}. The results are shown in Table 5. Case I is based upon the light scattering coefficient apportioned using the results from multiple regression. The constant term a_0 in Equation (1) has been apportioned to each species in proportion to the contribution of that species to b_{sp}. Further, the coefficients a_i, which pertain to 475 nm wavelength light, were re-normalized by a theoretical factor of 0.8 so that the extinction budget would pertain to light of wavelength 550 nm. The theoretical factor is the mean ratio of the scattering coefficients calculated from the aerosol size distribution for 550 and 475 nm light. For $(b_{apf}/M_f)_e$ we used the value $12.5\,m^2\,g^{-1}$ (Groblicki *et al.*, 1981). Cases II and III are based upon results obtained from the size distribution calculations assuming external and internal mixtures, respectively. Case IV is obtained for an assumed constant value for b_{sp}/M_f of $1.99\,m^2\,g^{-1}$ for each species (deduced for $\lambda = 550\,nm$ from the ratio of measured means in Table 4); for absorption due to fine particles we used the value $12.5\,m^2\,g^{-1}$.

The results for elemental carbon shown in Tables 2 and 5 present an interesting contrast. According to Table 2, elemental carbon's contribution to light scattering is highly dependent upon whether the mixture is internal or external. Yet, elemental carbon's contribution to light extinction depends only slightly on the type of mixture, because the dependence of scattering and absorption coefficients upon mixture type tend to cancel.

All methods considered indicate that about 82% of the light extinction in Denver is due to fine particles. However, the various methods for apportioning the contribution by fine particles to specific chemical species do not agree exactly. Until the differences can be explained by a physical model, the contributions to light extinction coefficient by specific chemical species are uncertain by a factor of two.

DISCUSSION

The results presented above illustrate the importance of evaluating statistical uncertainties in the apportionment of light scattering coefficients by chemical species using multiple regression. Although we used a fairly large data set containing 132 independent measurements, the resulting uncertainties were substantial. For each species, the 95% confidence

Table 5. Extinction budget by percentage for chemical species using various models at $\lambda = 550\,nm$

Component	Multiple regression Case I	Size distribution: External mixture Case II	Size distribution: Internal mixture Case III	Constant coefficient Case IV
Ammonium sulfate	10 ± 2	7	6	4.7
Ammonium nitrate	6 ± 2	10	10	6.7
Elemental carbon (fine)	46 ± 3	26	29	46.6
Elemental carbon (coarse)	4	4	4	3.8
Organic matter	12 ± 7	18	15	9.1
Remainder	9 ± 3	20	21	14.6
Nitrogen dioxide	8	9	9	8.7
Rayleigh	6	6	6	5.8

intervals for the light scattering to fine particle mass concentration ratios were as follows: ammonium sulfate ± 17%, ammonium nitrate ± 25%, elemental carbon ± 96%, organic matter ± 59% and remainder mass ± 29%. Of all the coefficients obtained by multiple regression, only that for ammonium sulfate is significantly different from the others. Thus, the assumption made by Heisler *et al.* (1980) that all species have the same scattering to mass concentration ratio is consistent with the multiple regression results for all species except ammonium sulfate.

None of our size distribution based calculations are able to account for the large coefficient of sulfate. However, a plausible explanation is as follows: Wolff *et al.* (1981) reported the presence in the Denver aerosol of an unknown sulfur species in addition to the water soluble sulfate. This 'excess sulfur' constituted 44% of the total sulfur measured by X-ray fluorescence and was found to be highly correlated with sulfate ($r = 0.89$). Because of this high correlation, the excess sulfur and any related oxides or ions not included for in the sulfate term in the regression equation (1) would manifest themselves as an increase in the regression coefficient for sulfate. The reported large amount of excess sulfur (44%) may be a result that is unique to the sampling site for which the data that we used were obtained. At other sites in Denver the amount of excess sulfur was less than 15% of the total sulfur (Heisler *et al.*, 1980). At three sites in the eastern half of United States, no excess sulfur was detected (Stevens *et al.* 1978, 1980; Dzubay *et al.*, 1982).

The scattering coefficient for nitrate deduced by multiple regression is 35% smaller than the values calculated theoretically. We doubt that this is due to bias in the nitrate concentrations used in the regression analysis even though there are known possibilities for bias in nitrate measurements. No positive sampling bias could have occurred because the nitrate data were obtained using inert Teflon filters (Countess *et al.*, 1980). A negative bias could have been caused by a reaction between acid sulfate and ammonium nitrate particles on the filter (Harker *et al.*, 1977) or if nitrate particles evaporated after sampling (Shaw *et al.*, 1982). However, a negative bias in the nitrate concentration would have caused the regression coefficient to be too high, which is opposite of that seen in Table 2.

The smaller value of scattering coefficient predicted for carbon in an internal mixture is accompanied by a much larger value for the absorption coefficient per unit carbon mass concentration as compared to an external mixture. As a result, the total extinction coefficients per unit mass concentration for internal and external mixtures are the same within 6%. This result does not depend significantly on the formula that we used for computing the average imaginary refractive index or the amount of void spaces that we assumed were in the particles.

Before we can determine which model gives the best apportionment of extinction coefficients, we need to know more about the nature of the 'excess sulfur' found by Wolff *et al.* (1981). We also need to determine if there is a physical basis for the difference in sulfate results by multiple regression and integration of size distributions. In addition, we could get more meaningful results from size distribution-based calculations once the physical nature of the aerosol is better known. In the present calculation we have assumed the extreme situations of external and internal mixtures. While such assumptions give insight into the nature of the species' dependence of the scattering coefficient per unit mass concentration, the actual aerosol particles may consist of chemical mixtures that are neither purely internal nor external. Our calculations for an internal mixture were based upon the assumption that we could apply simple Mie theory to particles using composition-weighted average values for the density and refractive index. Further knowledge about the scattering properties of particles containing a mixture of chemical species is required to determine the accuracy of such an assumption. Furthermore, the Mie theory applies to spherical particles, while the particles in Denver are agglomerates. Although Ackerman and Toon (1981) have suggested that the effect of the nonsphericity of the particles may be small, further investigation is necessary.

Acknowledgements—We thank George Wolff and Peter Groblicki of General Motors Research Laboratory for useful discussions and for generously providing their experimental data. One of the authors (H. Hasan) acknowledges a research associateship from the National Research Council, U.S. National Academy of Sciences.

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